THERMAL DONORS IN BORON-IMPLANTED Cz-SILICON. PHOTOLUMINESCENCE STUDIES*

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Thermal donor generation process is studied in heat-treated (450–500°C, 1 min–100 h) boron-doped pulled silicon by low-temperature photoluminescence. The well-known P and H emission bands related to thermal donors are distinguished. The influence of 10^{15} cm^{-2} 150 keV boron implantation on the photoemission spectra is investigated. For "as implanted" and short-annealed ($T_{ann} < 5$ min) samples some radiation damage bands can be observed. The intensity of P and H emission bands is then studied versus the annealing time. Pronounced enhancement of thermal donor formation rate is clearly concluded, with maximum concentration peaking by $T_{ann}^{max} < 1$ h, while for non-implanted material by $T_{ann}^{max} \gtrsim 100$ h. On the basis of experimental results the idea of thermal donors involvement in the reverse annealing phenomenon for boron implants in silicon is strongly supported.

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Boron-implanted Cz-Si structures are commonly used in semiconductor technology. Therefore, characterization and elimination of grown-in and process-induced defects in such structures became important. Here, the so-called "reverse annealing" still remains a puzzling experimental phenomenon [1–4]. It is observed as an unexpected decrease of conductivity for certain annealing temperature region, while for still higher temperatures the annealing curve regains its common increasing character until the conductivity of the implanted structure reaches its maximum value determined by implantation and substrate parameters.

The origin of the reverse annealing is not fully understood. Until recently, it was generally assumed that the decrease of substitutional boron contents which is responsible

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for the conductivity drop is the result of interaction with silicon selfinterstitials. The reaction would then involve the exchange mechanism as proposed by Watkins [5]

$$\text{radiation damage} \xrightarrow{\text{annealing}} \mathrm{Si_I};\ \mathrm{B_{SUBST}} + \mathrm{S_I} \rightarrow \mathrm{B_I}.$$

The reaction could take place only in a certain temperature region determined by the thermal stability of those defect complexes which are able to release selfinterstitials.

However, such a relatively simple mechanism faces several difficulties the most severe one being the mismatch of the concentrations of the involved boron substitutionals on one side and selfinterstitial complexes on the other. It also fails to explain several peculiar experimental observations such as:

— the reverse annealing is observed only for boron implantation, while the replacement mechanism is known to be effective also for other group III elements [5],

— borons leaving silicon host lattice sites within the reverse annealing temperature region do not take random interstitial positions (as they do for the high-temperature proton irradiation) but they take positions along ⟨110⟩ atomic ions [6].

In view of the above mentioned difficulties the possible oxygen involvement in the reverse annealing has recently been suggested [7]. Indeed, the possibility that the presence of oxygen in the silicon substrate may play an important role is strongly supported by the existing experimental evidence:

— the oxygen concentration was found to influence directly the annealing behaviour of the radiation damage [8] as well as the initial substitutional boron contents for "as implanted" samples,

— the reverse annealing was reported to appear in Cz-Si and there seems to be no evidence for its occurrence in FZ silicon.

Interstitial oxygen, which is present in Cz-Si in concentrations 5×10^{17}–1×10^{18} cm^{-3}, tends to form clusters known as thermal donors. The actual concentration of thermal donors which could be achieved in the implanted layer is of crucial importance for the justification of their possible involvement in the reverse annealing.

Thermal donors are created upon annealing in 320–500°C temperature range, their formation rate peaking at 450°C. The usual values of the formation rate are within 10^{11}–10^{12} cm^{-3}s^{-1} range and therefore, to obtain significant concentrations of thermal donors heat treatment must be prolonged for long periods of time. However, it has recently been suggested [9] that for strongly p-type material both, the formation rate and the maximum concentration of the thermal donors would be enhanced. Then, considerable numbers of the oxygen clusters would be formed even within a short annealing time.

To verify whether thermal donors could be held responsible for the "reverse annealing", heat treatment of boron-implanted Cz-Si wafers has been performed. The formation of thermal donors was monitored by their photoemission bands known as P and H lines [10]. The photoluminescence experiment was chosen here because of its high sensitivity and good applicability to thin surface layers.

The luminescence was excited with an Ar$^+$ ion laser, dispersed by Jobin Yvon f/12 monochromator and detected with a 77 K cooled Ge detector. The samples were immersed in liquid helium. The experimental results are shown in Fig. 1 where relative intensities of P and H lines are plotted against the 450°C annealing time. Also, the relative intensities of the radiation-damage emission bands C and I_2 are presented. A spectacular enhancement may be noticed, with the thermal donors concentration peaking for $\sim t = 10$ min. while for nonimplanted wafers P and H emission bands could be observed only after prolonged heat-treatment times (100 h).

The experiment clearly shows that boron implantation leads to remarkable increase of thermal donors formation rate. It proves that even after short annealing times thermal

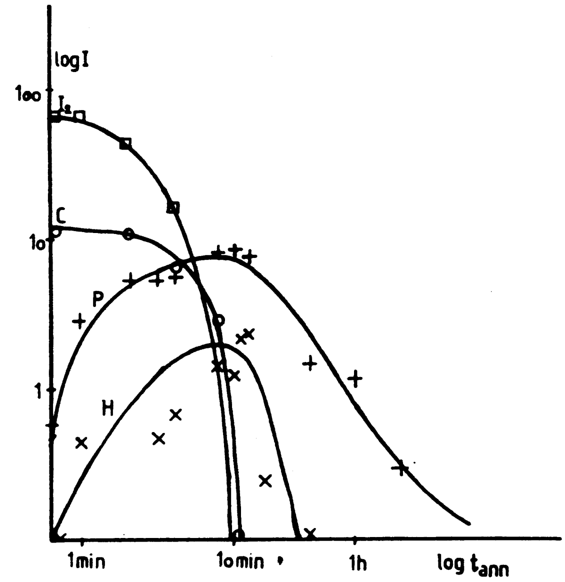

Fig. 1. The intensity of photoluminescence emission bands versus the annealing time (T_{ann} = 450°C): thermal donors: + – P line 0.7667 eV, × – H line 0.9259 eV; radiation damage: ○ – C line 0.7894 eV, □ – I_2 line 1.080 eV

donors are present in large concentrations within the implanted layer and therefore could account for the reverse annealing.

The actual way in which the substitutional boron concentration can be influenced by the growth or by the presence of thermal donors may only be speculated upon. The possibility that acceptors might directly be involved in the creation of thermal donors has already been considered [11]. It receives direct experimental support since both, thermal donors formation rate and their thermal equilibrium concentration were found to depend on the acceptor concentration [9] and on the acceptor itself [12]. It could also explain the ⟨110⟩ arrangement of borons displaced from their lattice positions which could then be incorporated in the structure of thermal donors [13] and not just dispersed in random way. However, none of the recently published models for thermal donors [14, 15] considers the possibility of direct acceptor incorporation in the structure of thermal donors.

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